

Interactive comment on “Evolution of NO₃ reactivity during the oxidation of isoprene” by Patrick Dewald et al.

Anonymous Referee #2

Received and published: 9 June 2020

The authors report on studies of NO₃ reactivity during ‘nighttime’ experiments in the SAPHIR chamber, with a primary focus on isoprene chemistry. An FT-CRDS system is used to determine the NO₃ reactivity with respect to stable products in the chamber, while a box model analysis is used to assess additional NO₃ losses (reaction with peroxy radicals, chamber wall losses) not determined by the FT-CRDS system. Among the key findings are the following: the FT-CRDS accurately measures the NO₃ reactivity towards isoprene, and functions well under the conditions studied; stable products of the NO₃/isoprene chemistry do not contribute significantly to NO₃ reactivity; the generic (and highly uncertain) RO₂ + NO₃ rate coefficient may be a factor of two or more higher than current estimates. Overall, this is a very solid paper that certainly is publishable in ACP. The paper is well written, and assumptions and uncertainties in the

C1

measurements are generally presented in detail. A few questions and suggestions are presented below for the authors to consider.

There are assumptions and caveats associated with equation (1), line 220 – Could there be significant reaction products that the PTR-MS is unable to detect? Could some products not make it into the flow tube for detection by the k(NO₃) instrument? NO₃ losses due to chamber walls and radicals are not measured by the k(NO₃) instrument. Most (or maybe all) of these are dealt with at different points in the manuscript, but a clear statement or two delineating these at this point might be helpful to the reader.

Can the authors be more quantitative regarding the b-caryophyllene expt (Fig 3a)? - e.g., What is its expected lifetime? The k(NO₃) instrument is clearly not seeing the full impact of the stated addition of 2 ppbv b-caryophyllene.

Line 265 / Fig 3b: Isoprene loss here is due to reaction with O₃, I assume (maybe also OH formed in the ozonolysis)? Does the agreement noted between the k(NO₃) instrument and the k[isoprene] calculation imply that major isoprene ozonolysis products are also comparatively unreactive towards NO₃? (Also, a minor detail, but the isoprene decay seems more rapid than would be implied by the O₃ concentration given?)

Line 312 or so - It should be noted here that NC₄CHO is only one of many products that can be formed.

In Figure 9, it is not clear to me that the increased RO₂ + NO₃ rate coefficient improves the model/measured NO₃ comparison?

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-360, 2020.

C2